Science World Journal Vol. 15(No 4) 2020
www.scienceworldjournal.org
ISSN: 1597-6343 (Online), ISSN: 2756-391X (Print)
Published by Faculty of Science, Kaduna State University

Full Length Research Article

METAL ORGANIC FRAMEWORKS SUPPORTED WITH EMIRALDINE MODIFIED GRAPHITE ELECTRODE FOR AMPEROMETRY DETECTION OF HERBICIDE

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ABSTRACT
The use of herbicide to destroy unwanted weeds by famers have created harmful environment for humans due to incomplete degradation of herbicides in the soil. The residue is washed into rivers during surface runoffs and consumed by humans. This requires the chemist to develop a sensor for detecting herbicides in there smallest availability in drinking water. In this work, a Polymer and Metal Organic Frameworks Graphite Electrode was developed for the detection of herbicide. These was achieved by homogenizing Emiraldine, Hkust and Graphite in a ratio 1:1:4 respectively in a mortar and pestle and then packed tightly into a 3 mL syringe using a copper wire as contact medium between chemical composite and the electrical setup to achieve and electrochemical reaction at the electrode interface. The interfaces serve as the redox mediator for electron transfer. Scanning Electron Microscopy was used to study the morphology of the electrodes. The modification of the surface of developed carbon paste sensor with Emiraldine and Hkust-1 greatly improved the detection of the atrazine on the sensor with a working linear range of 0.4 – 1.0 µM and low detection limit of 0.09 ± 0.67 µM at pH 5 and scan rate of 50 mV/s. The modified electrode turned out to be highly stable and selective its amperometric behavior. Importantly, this method provided a promising electrochemical sensing platform for atrazine analysis and its detection for human safety.

Keywords: HKUST-1, Emiraldine, Graphite, Amperometry and Atrazine

INTRODUCTION

Agricultural activities which are of great importance have become a major threat to the environment. Because of the infertility of the soil that has undergone cultivation over the years, farmers have resulted to different forms of soil nutritional therapy to make the soil fertile for cultivation. It is no longer news that herbicides are used to kill broad leaved weeds and even shrubs before and during cultivation. As much as the use of herbicide has disadvantages, it also has advantages like creating a stress free, easy way of getting reed of weeds around the environment and minimizing survival of the fittest between wanted and unwanted crops (Metteo *et.al* ., 2019).

Atrazine, a largely used herbicide by farmers has widely been studied to have a lone time residual effect. Atrazine herbicide residues may enter the food chain through air, water, and soil. They affect ecosystems and cause several health problems to animals and humans since they remain in the soil for a long time say (40 years) without degradation. They can produce infertility, and immunological and respiratory diseases (Tomlin, 2009).

To solve the problems created by these used herbicides, Chemist have developed sensors for the detection of these herbicides. Detection of Atrazine herbicides at the levels established by the Environmental Protection Agency (EPA) remains a challenge. Chromatographic methods coupled to selective detectors have been traditionally used for atrazine herbicide analysis due to their sensitivity, reliability, and efficiency. Nevertheless, they are time consuming and laborious, and require expensive equipment and highly trained technicians. Thus, there is a great necessity for new analytical methods with better precision, accuracy, sensitivity, and selectivity. These methods must not be prohibitively expensive and, ideally, could be adapted for measurement in the field. In this regard, electrochemical sensors are advantageous. Over the past decade, considerable attention has been given to the development of sensors for the detection of Atrazine herbicides as a promising alternative (Tang. 2006; Dhand. 2011).
Among the carbon sensors, the graphite electrode (GE) is of particular importance. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface, and low cost are some advantages of GEs over all other carbon electrodes. Therefore, GE can provide a suitable electrode substrate for preparation of electrodes. But due to the drawback of graphite electrode in the electro analysis of atrazine detection, GEs are being modified with other material such as polymers (Tesfaye, 2016).

A polymer sensor is a self-contained device that integrates a polymer that recognizes the analyte and a transduction element used to convert the (polymer) chemical signal resulting from the interaction of the analyte with the polymer receptor into an electronic one (Dhand, 2011). Electrochemical transducers have been widely used in sensors for herbicides detection due to their high sensitivity (Jaffre, 2001; Luque *et.al*., 2003; Andreescu *et.al*., 2006). Additionally, their low cost, simple design and small size make them excellent candidates for the development of portable sensors (Thevenot *et.al*., 1999; Freire.*et.al*., 2003; Grieshaber.*et.al*., 2008) according to the polymer recognition element, polymer sensors have been developed for herbicides detection.
In this work, GE for atrazine detection with metal organic frameworks (HKUST-1) a coordination polymer and Emiraldine is also called an ideal metal because it is an electroactive polymer.

MATERIALS AND METHODS

Reagents

In this work all modifiers were purchased from Sigma-Aldrich (of analytical grade) and used without further purification: Emiraldine, MOF-199 (HKUST-1), Animal charcoal, Ethanol (EtOH), Ethanol,

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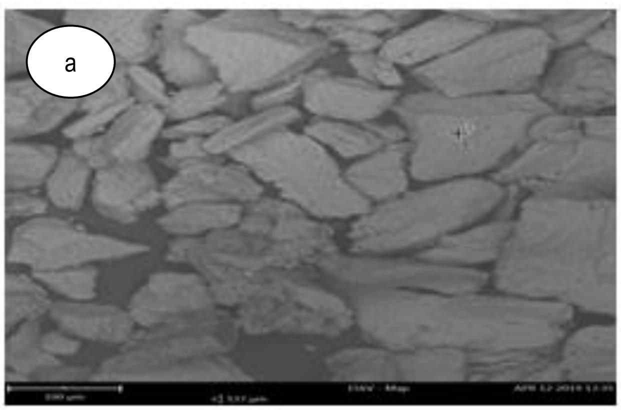
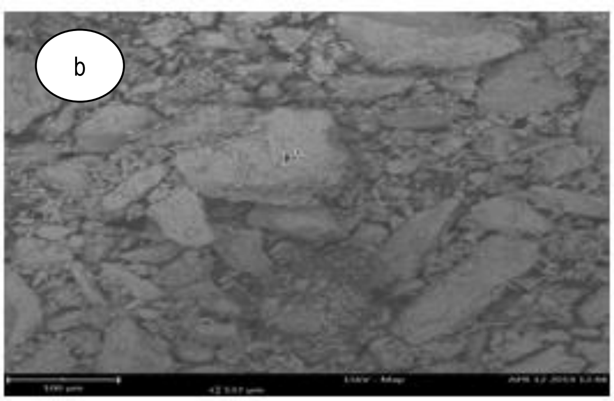
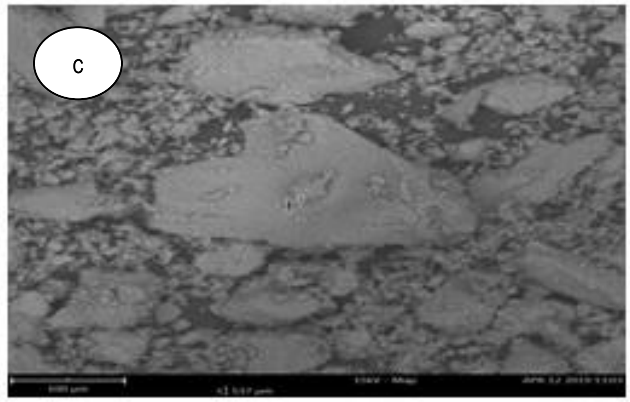
Hydrochloric acid (HCl)(Alpha), Sulfuric (H_2SO_4)(Fisher chemicals, United Kingdom)

Amperometric Experiments
To prepare the composite, animal charcoal mixed with Emeraldine and Hkust-1, (200mg) Emeraldine powder and 200 mg of Hkust-1 were mixed with animal charcoal (800 mg) in the ratio 1:1:4 and the mixture was transferred to the mortar and pestle and then homogenized. The composite was packed into electrode assemblies made from 3 mL plastic syringe of 2.3 mm outer diameter using spatula and smoothened on a glass slide surface. Electrical contact was made with a copper wire through the syringe (Tesfaye *et.al*., 2016). After the electrode was fabricated, a stock solution containing (0.32 mM) atrazine was prepared. 5 ml volume of the working solution was transferred to 10 mL vail which was used to rum a cyclic voltammogram of the effect of scan rate from 10 -90 mV/s and the effect of pH of 1-8. Since amperometry under stirred condition is much more sensitive than cyclic voltammetry and it is important for developed electrodes, this method was employed for detecting atrazine even at much lower concentrations. Prior to the optimization of the ideal condition to which the electrodes were run in a ferrocyanide to check its working potential at a scan rate of 100 mV/s

RESULTS AND DISCUSSION







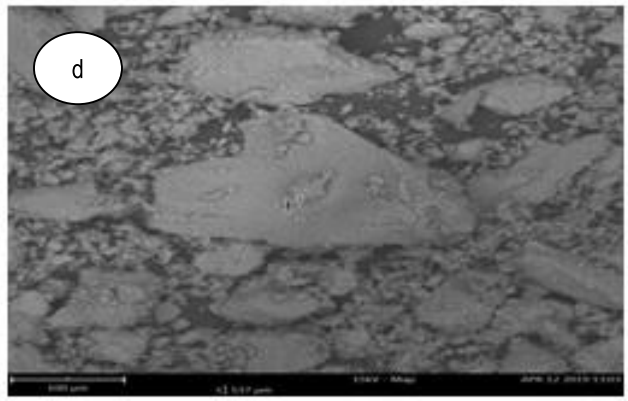


Plate: SEM morphology of (a) Bare Graphite Electrode (b) Graphite with Emiraldine (c) Graphite with Hkust -1 and (d) Graphite with Emiraldine and Hkust-1

SEM was used to study the morphology of the electrodes. Figure (a) clearly shows a different morphology to others showing the presence of fibers of emiraldine in (b) and presence of Hkust in (c) and more compacted in (d) because of the mixture of (b) and (c). This is because only graphite is compacted in that electrode but figure b, c and d show like morphology as a result of the modification with emeraldine and Hkust which shows how the polymers are tightly packed within and around the graphite.

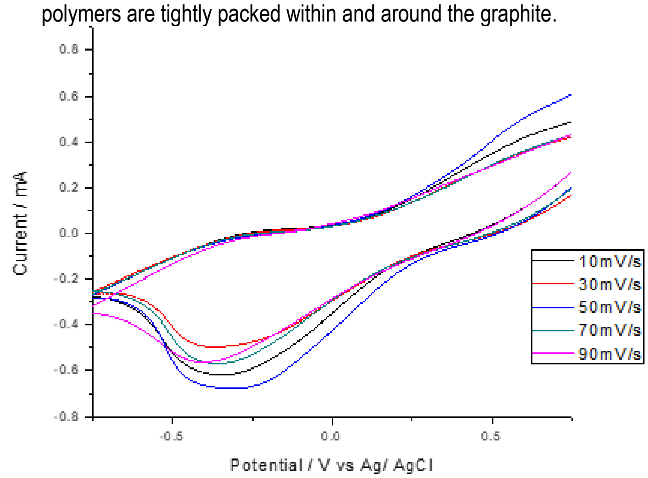


Figure 1: Cyclic Voltammogram showing the effect of scan rate of 10-90 mV/s in 0.32 mM atrazine solution at (pH 3) supporting electrolyte.

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Figure 1 shows the modified electrode potential ramps linearly versus time in cyclical phases and voltage change over time during each of phase. Cyclic voltatametry data was used to provide information about redox potentials and electrochemical reaction rates**.** Figure 1 shows the effect of scan rate running at increasing scan rates. Upon increase in scan rate, the reduction of atrazine increases until at 50 mV/s which was the best peaks around the potential of atrazine which is 50 mV/s according to literature (Tefaye, 2016).

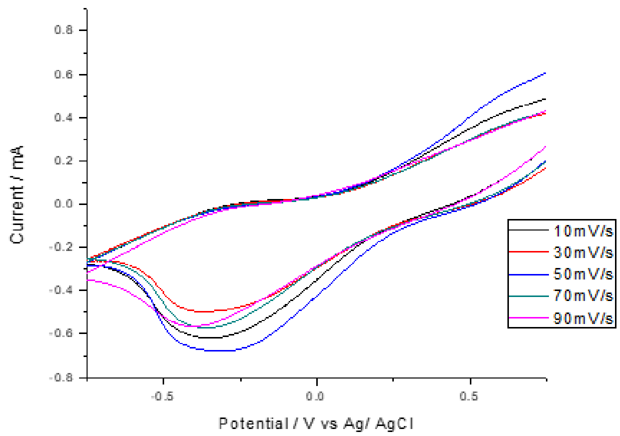

Figure 2: Cyclic voltammogram of the effect of pH on emiraldine/Hkust modified electrode of 0.32 mM atrazine pH value at 1.0 – 8.0 ran at scan rate of 50 mVs^{-1}

pH is an important parameter in absorption as it affects both the degree ionisation of the sorbate and the surface charge of the sorbent during the adsorption process. Figure 2 shows the effect of pH on the modified electrode. The best peak is at pH 5 because at pH above 5 it was clear that the reduction of atrazine at the electrode started to shift far from the reduction potential of atrazine which simply shows that there was starting to be interference by the peaks of hydrogen ions. At pH 5 the electrode showed the potential to detect atrazine

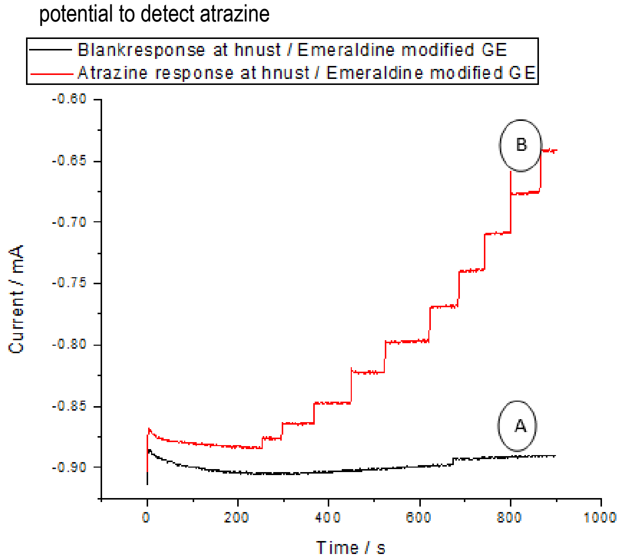

Figure 3: A- current –time response of successive additions of atrazine at modified electrode at pH 5

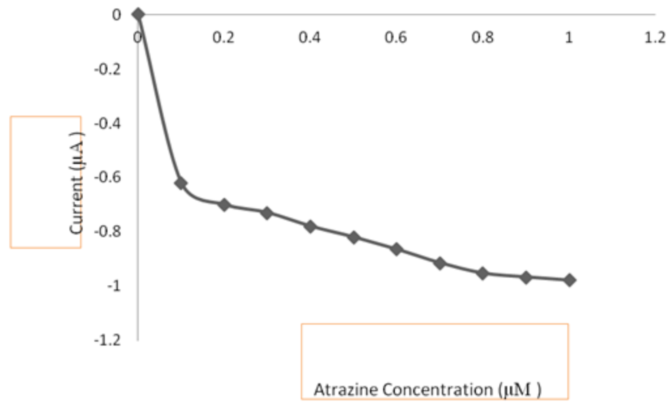

Figure 4: shows the effect of atrazine concentration

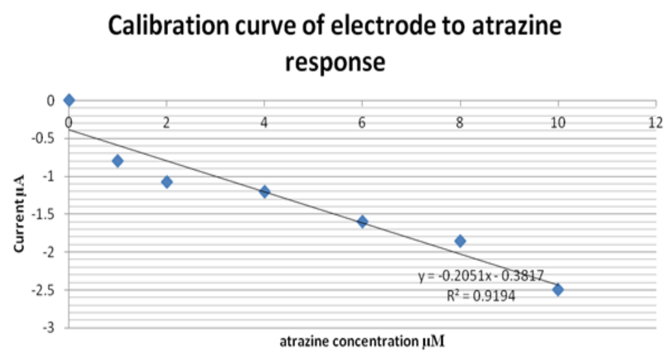

Figure 5: Calibration curve of successive additions of atrazine responses at modified electrode in 0.32 mM of atrazine solution at pH 5 at scan rate of 50 mV/s

As to using the modified electrode, various spiked atrazine concentrations of 0.1 – 1.0 µM from 0.32 mM of atrazine using Amperometry were obtained in (Fig: 3b) and running amperometry of buffer as the blank in fig 3a. It shows that current increased with increase in atrazine concentration with a linear range 0.4 – 1.0 µM and with the regression equation also in accordance with the literature (Metteo, 2019) Fig 3, 4 and 5. The concentration found with the proposed method is to a low detection limit (LOD) of 0.09 ± 0.67 µM.

Conclusion and Recommendation

In this work, a sensor was developed from immobilizing graphite assisted with emeraldine and Hkust polymers. Modification was simple as well as homogenizing to compact into the syringe. The modified electrode shows linearity in the detection of atrazine upon injection of different concentration and detecting atrazine at a very low detection limit of 0.09 ± 0.67 µM. Electrode response was very selective to atrazine at its specific potential there by making. This electrode is recommended for real samples analysis.

Acknowledgement

My sincere gratitude goes to **Tertiary Education Trust Fund** (TETFUND) for making available the grant to carry this research.

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